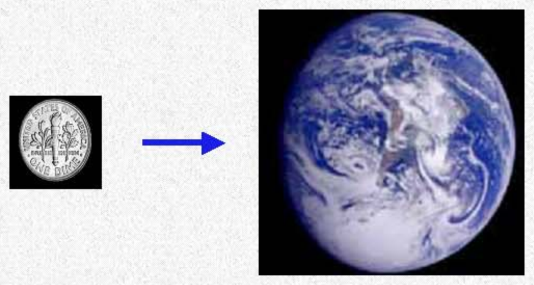
Novel Metal Alkoxides for Use as Precursors to Complex Ceramic Nanoparticles

Timothy J. Boyle, Mark A. Rodriguez, Thomas Headley, Miguel Trujillo, Nicholas L. Andrews, Scott D. Bunge,

Introduction

Nanoparticles are materials ranging in size from about 1 to 100 nanometers but most often refer to discrete particles below 50 nm in size. The proposed changes in physical properties expected for materials in this size regime drive the research interest in these materials.

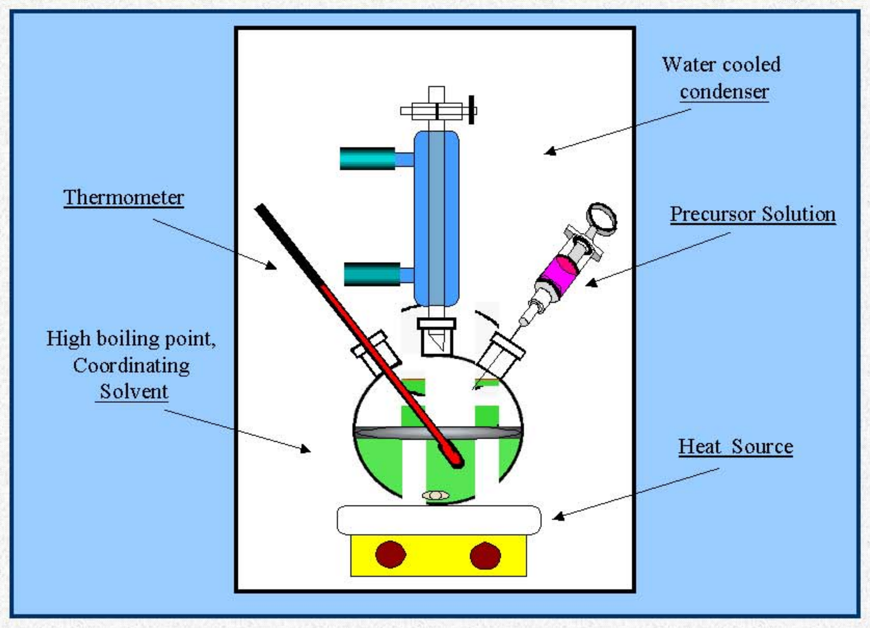


*A nanometer is to a meter what a dime is to the planet earth

Nanoparticles of noble metals have been used for hundreds of years (i.e., stained glass used Au nanoparticles as a red coloring agent in the Middle ages). However, only recently has there been a concerted effort to synthesize a wide range of nanomaterials with controlled properties (i. e., size, shape, composition).

General Synthesis of Nanoparticles

A general scheme of how nanoparticles are currently synthesized is shown below. In this process a precursor solution is injected into a hot solution that contains the coordinating solvent This yields a supersaturated solution and at high enough concentrations a nucleation shower occurs forming crystals.



If allowed to heat at this temperature, La Mer growth may occur yielding larger particles. Therefore, the time and temperature of these reactions are closely monitored and critical in the formation of crystalline monodispersed species. The precipitate is collected by centrifugation and washed to remove excess surfactant after the reaction is complete.

Single-Source Ceramic Nanoparticles

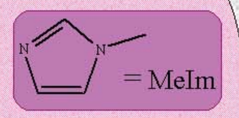
While there is an abundance of literature on ceramic nanoparticles, but there are very few reports available for complex oxide nano species. Due to the widespread electronic applications of ceramic materials, investigation of multi-cationic ceramic nanoparticles are of current interest for the development of smaller devices and investigation of the fundamental physical properties.

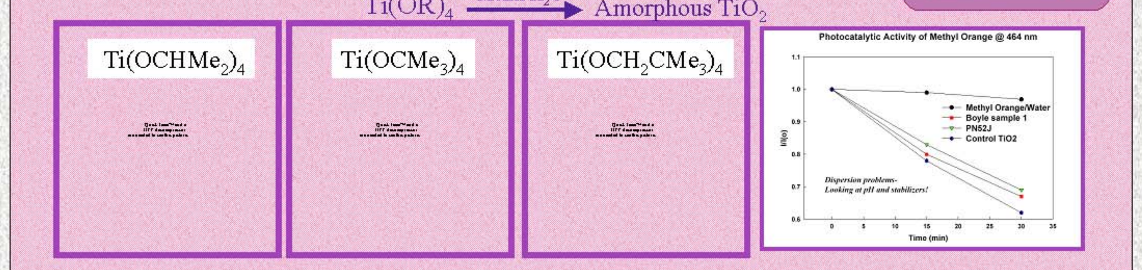
Single-source precursors will be of much more utility for nano-production than for sol-gel techniques due to the rapid decomposition of the starting materials for nanomaterials synthesis. If the proper precursors can be developed the stoichometry will be built into the molecules which are often rapidly converted to the nanoparticles. Further, a uniform decomposition is more likely to occur since it is a single molecule, forcing a homogenous product. Metal alkoxides are of interest as precursors due to their low conversion temperatures, low carbon contamination, and relative ease of modification. However, controlled construction of mixed metal alkoxides have not been realized. We discuss the synthesis of several novel metal alkoxides and their utility in a novel thermal decomposition route that we have recently developed.

This work supported by the Department of Energy, Office of Basic Energy and Science and the United States Department of Energy under contract number DE-AC04-94AL85000. Sandia is a multi-program laboratory operated by Sandia Corporation, a Lockheed-Martin Company, for the United States Department of Energy.

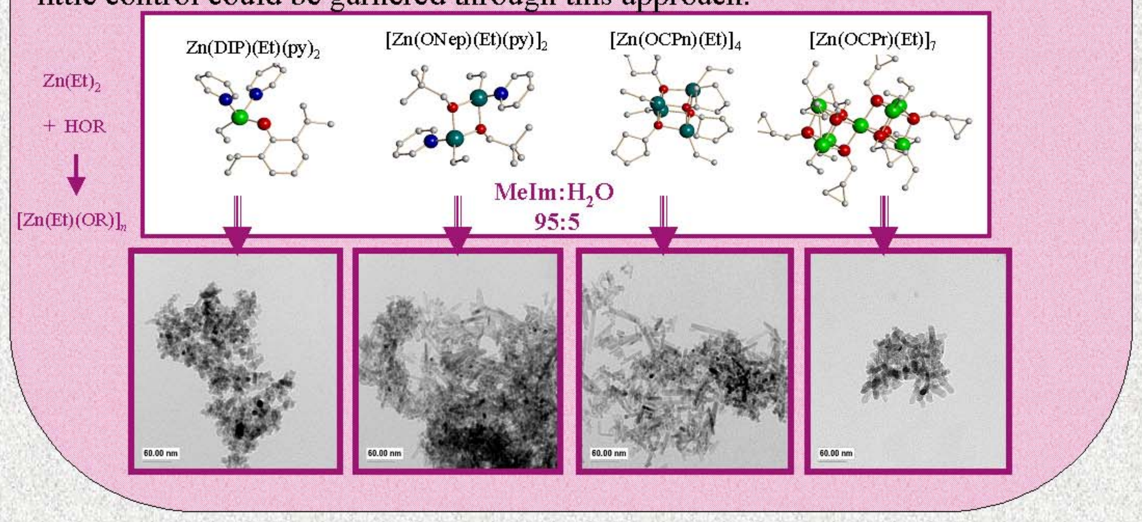
Homonuclear Ceramic Nanoparticles

TiO_2 nanoparticles were successfully generated using a MeIm/H_2O solution route. Useful for photocatalytic decomposition of organic species.





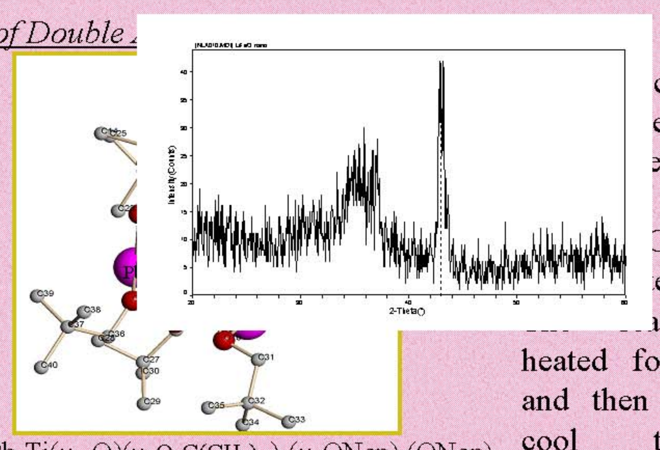
ZnO has numerous electronic applications. Investigation of precursor construction on final morphology using the MeIm/H_2O solution route revealed little control could be garnered through this approach.



PbMO$_3$ "Single-Source" Precursors

Synthesis of Double Alkoxide Precursors

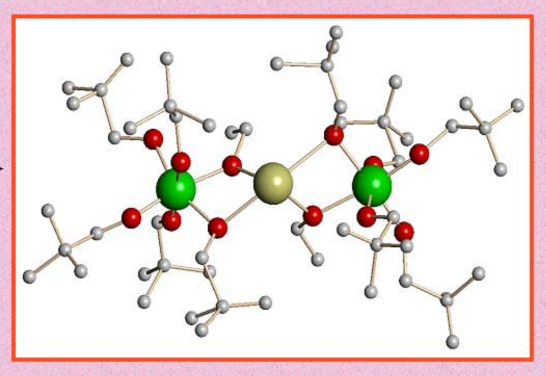
2 "Pb(ONep)$_2$" + [Ti(μ-ONep)ONep)$_3$]$_2$ + HO$_2$C(CH$_3$)$_3$ →



$Pb_3Ti(\mu_3-O)(\mu-O_2C(CH_3)_3)_2(\mu-ONep)_3(ONep)$

ONep = OCH$_2$C(CH$_3$)$_3$

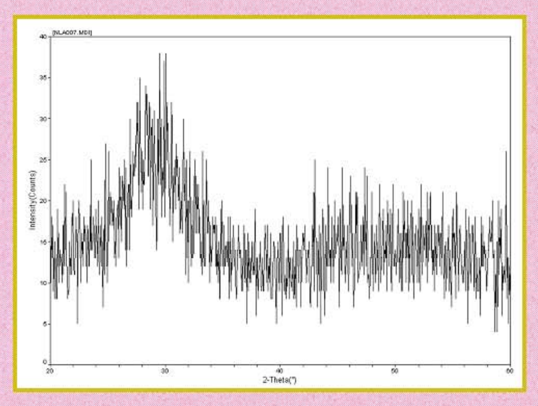
2 "Pb(ONep)$_2$" + [Nb(μ-OEt)ONep)$_3$]$_2$ →



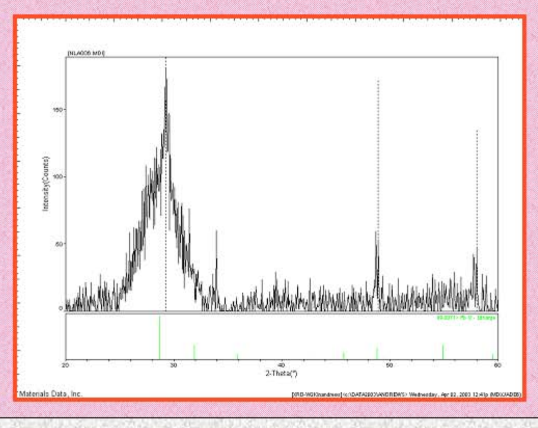
$PbNb_2(\mu-OEt)_2(\mu-ONep)_2(ONep)_6$

...cursors were ...ed in toluene ...en rapidly ... into a ...O solution at ...emperatures. ...action was heated for 1/2 hour and then allowed to cool to room temperature. After this time, the reaction mixture was centrifuged and the resultant precipitate was washed with hexanes and allowed to dry.

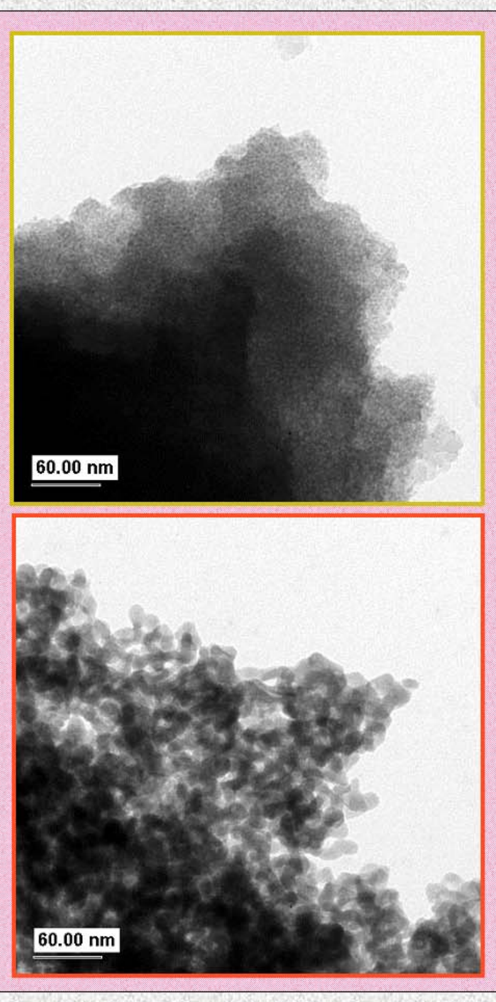
Characterization of Nanoparticles



XRD of nanoparticles synthesized from the Pb-Ti$_3$-alkoxide precursor and then fired at 450 °C, indicates that the material remains amorphous.



XRD of nanoparticles synthesized from the Pb-Nb$_2$-alkoxide precursor, indicates crystalline material was formed. The large broad peak and two smaller peaks implies either a very large aspect ratio or mixed phases are present



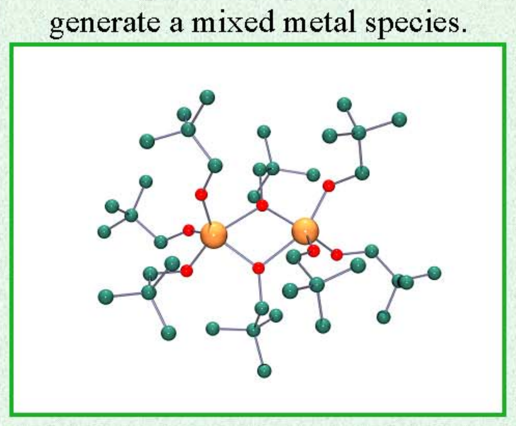
For both systems TEM images indicate that nano-particles were formed and XPS indicates that mixed cation are present for each sample. Clustering of the particles is occurring. Possibly stronger surfactants than MeIm will be necessary to fully disperse these particles. Higher processing temperatures will be necessary to fully crystallize these species.

(Ba,Sr)TiO$_3$ "Single-Source" Precursors

A great deal of interest lies in the tunable dielectric material (Ba,Sr)TiO$_3$ for microwave applications. Smaller highly crystalline material are of interest to generate smaller devices.

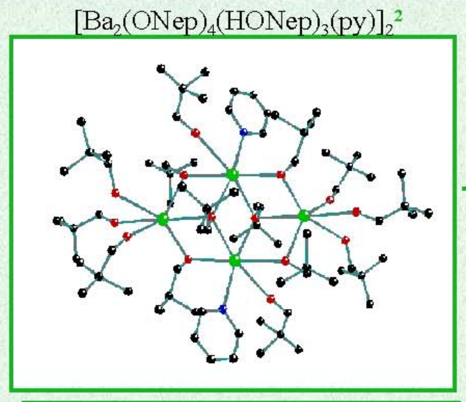
Synthesis of Double Alkoxide Precursors

The novel Ti-neo-pentoxide was independently mixed with the Ba or Sr neo-pentoxide precursor to generate a mixed metal species.

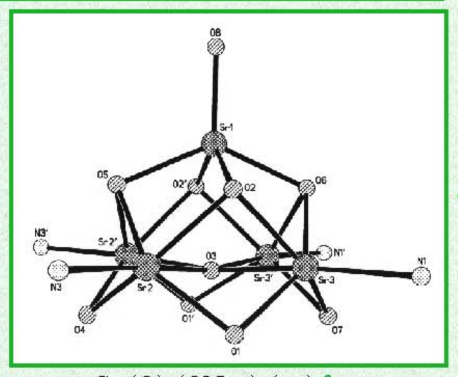


[Ti(μ-ONep)ONep)$_3$]$_2$[1]

$[Ba_4(ONep)_8(HONep)_3(py)]_2$[2]

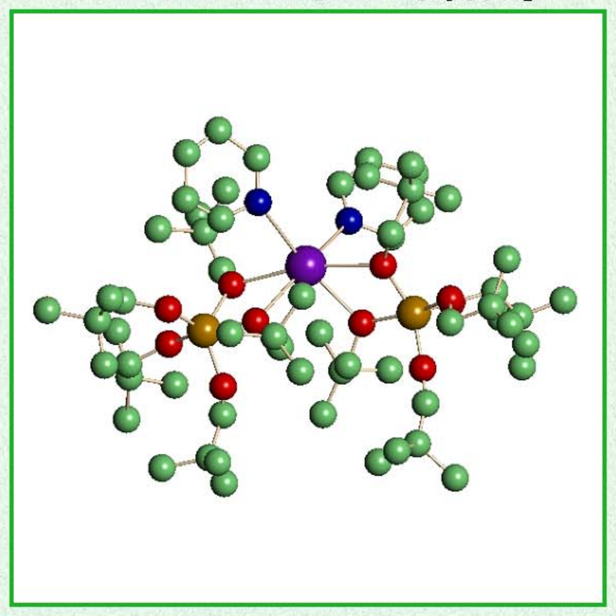


The individual precursors oligomerize due to the low charge to size ratio forming the mixed metal precursors.



$Sr_5(O)_2(ONep)_8(py)_4$[3]

Ba[Ti(μ-(ONep)(ONep)$_3$(py)]$_2$[2]



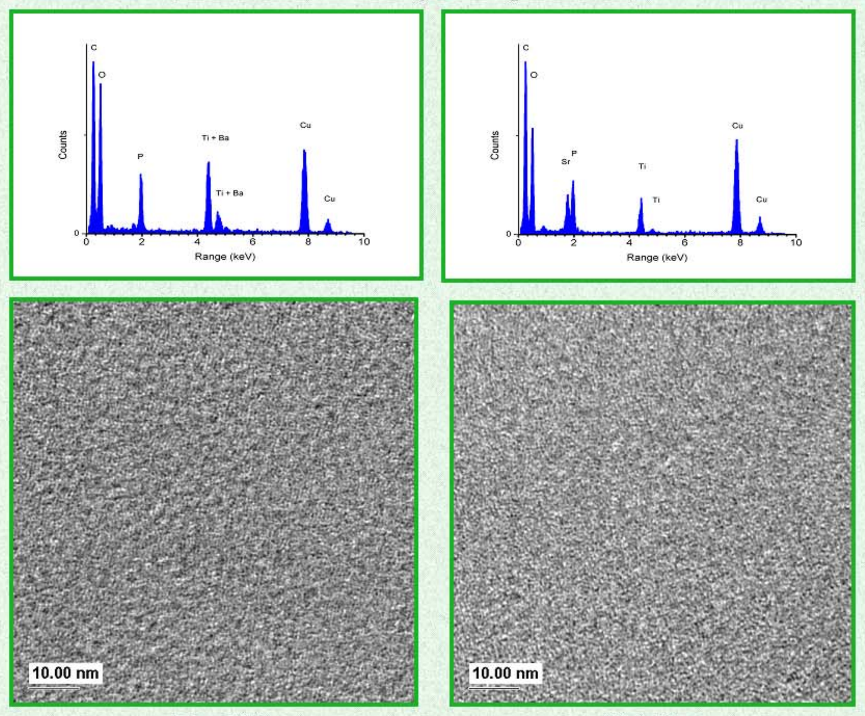
Sr[Ti(μ-(ONep)(ONep)$_3$(py)]$_2$[2]

The structure of the two congeners is identical forming the mixed metal species: M[Ti(μ-(ONep)(ONep)$_3$(py)]$_2$ where M = Ba, Sr (shown)[2].

1. Boyle, TJ; Alam, TM; Mechenbier, ER; Scott, BL; Ziller, JW. INORGANIC CHEMISTRY, JUL 16 1997, v 36, no 15, p 3293-3300
2. Boyle, TJ; Clem, PG; Rodriguez, MA; Tuttle, BA; Heagy, MD. JOURNAL OF SOL-GEL SCIENCE AND TECHNOLOGY, OCT 1999, v 16, no 1-2, p 47-55
3. Boyle, TJ; Tafoya, CJ; Scott, BL; Ziller, JW. JOURNAL OF COORDINATION CHEMISTRY, 2000, v 51, no 4, p 361-378

These multi-cationic species were dissolved in py and then injected into numerous surfactants. Most formed nanoparticles but none proved to be crystalline. Shown are the nanoparticles formed from a refluxing trioctylphosphine oxide (TOPO) solution.

Characterization of Nanoparticles



BaTiO$_3$ SrTiO$_3$

Nanoparticles were non-crystalline particles as determined by XRD and TEM but were on the order of ~ 2 nm in size.

LiCoO$_2$ "Single-Source" Precursors[1]

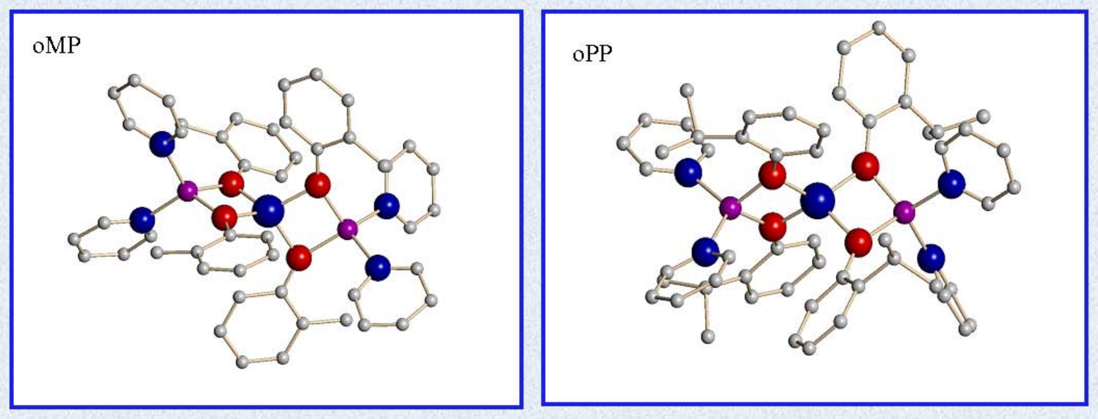
For Li ion batteries, LiCoO$_2$ is the cathode material of choice due to its high capacity (~ 130 m Ah/g). The higher the surface area the greater the capacity that is expected, therefore, surface dominated nanoparticles are of interest.

We have developed a novel family of single-source precursors for the production of LiCoO$_2$ nanoparticles. Using the MeIm/H$_2$O route we attempted to generate nanoparticles of LiCoO$_2$.

Synthesis of Double Aryloxide Precursors

Using an amide-alcohol metathesis route, we developed a novel family of aryl double aryloxide precursor for LiCoO$_2$. Two of these were chosen to investigate as precursor to nanoparticles and are shown below.

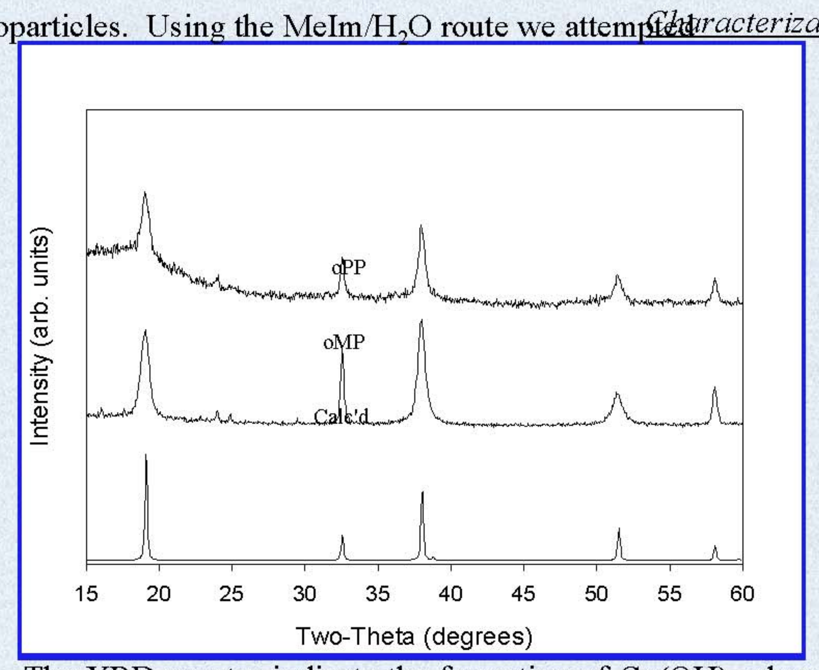
$$Co(NR_2)_2 + 2\ LiNR_2 + 6\ HOAr \xrightarrow{py} Co[Li(\mu\text{-}OAr)_2(py)_2]_2$$



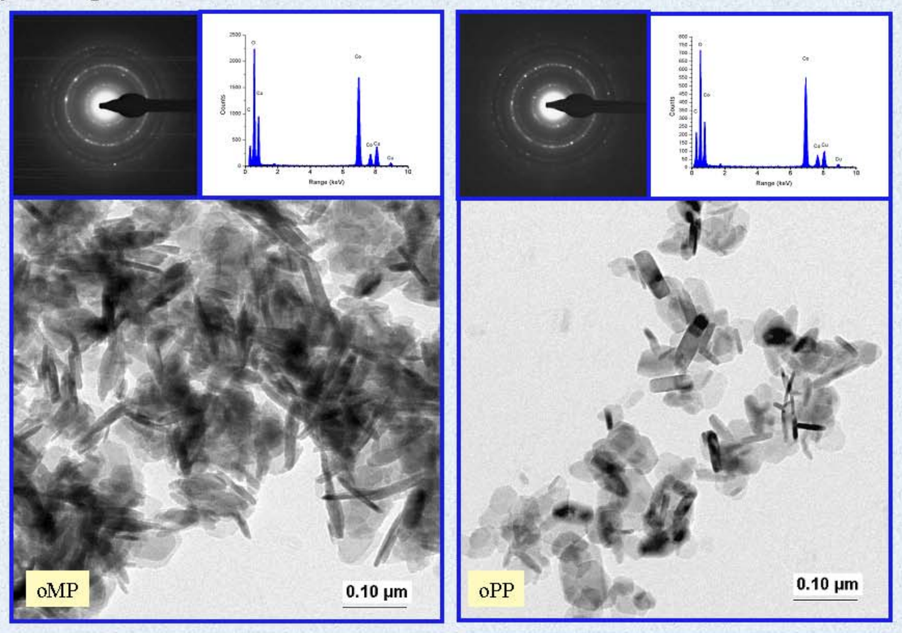
Dissolution of these precursors in pyridine followed by injection into refluxing methyl imidazole/water (95:5) led to the formation of nanoparticles.

1. Boyle, TJ; Rodriguez, MA; Ingersoll, D; Headley, TJ; Bunge, SD; Pedrotty, DM; De'Angeli, SM; Vick, SC; Fan, H. (submitted to Chemistry of Materials)

Characterization of Nanoparticles



The XRD spectra indicate the formation of Co(OH)$_2$ phase. The Scherer formula shows that the *c*-axis direction of the grain is in the ~10-20 nm range while the *a*-axis has a much larger dimension of ~60 -70 nm.

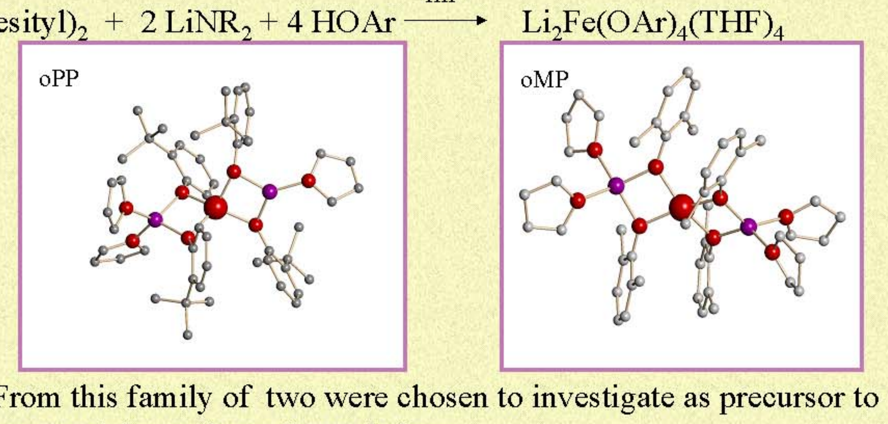


The nanocrystals were ~ 60-70 nm in size with a disk morphology. The nanocrystals have a large tendency to aggregate, which is not unusual for nanocrystalline metal oxides.

LiFeO$_2$ "Single-Source" Precursors

LiFeO$_2$ is of recent interest for use an alternative cathode material for Li ion batteries. We synthesized and characterized a novel family of aryloxides from an alkyl-alcohol exchange route.

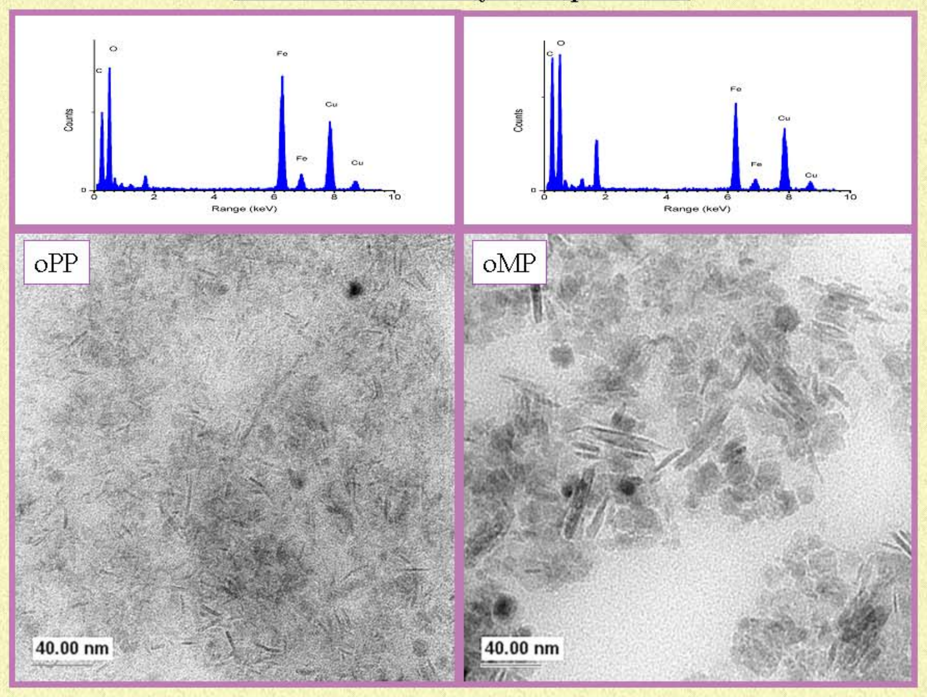
$$Fe(mesityl)_2 + 2\ LiNR_2 + 4\ HOAr \xrightarrow{THF} Li_2Fe(OAr)_4(THF)_4$$



From this family of two were chosen to investigate as precursor to nanoparticles and are shown below

Dissolution of these precursors in pyridine followed by injection into refluxing methyl imidazole/water (95:5) led to the formation of a precipitate which had both Li and Fe present. XRD is consistent with possible LiFeO$_x$ (layered oxide or spinel) phases.

Characterization of Nanoparticles



The nanocrystals were ~15-20 nm for the oPP and 15-35 nm for the oMP precursor. Both had disk and rod morphologies. XPS indicates Fe present but Li is difficult to detect.

Summary and Conclusions

- We have synthesized and characterized a number of novel families of homo- and hetero-geneous metal alkoxides based on the exploitation of the hyperoligomerization of these species.
- We have developed a novel route of nanoparticle synthesis using methylimidizole/H$_2$O. Wherein the MeIm is a high-boiling point, strong Lewis base that acts as the surfactant and the water hydrolyzes the metal alkoxides:

  (a) For monometallic ceramic species oxides and hydroxides have been isolated. (i.e., TiO$_2$ (amorphous), ZnO (crystalline rods). Determined precursor structure not as important in nanoparticle formation as for sol-gel routes.

  (b) Using single source Pb-M-alkoxides we have successfully generated nanomaterials some of which are crystalline.

  (c) Synthesized both BaTiO$_3$ and SrTiO$_3$ nanoparticles, but need to optimize system to obtain crystalline material.

  (d) Using LiCo-aryloxides we successfully generated crystalline, disk-shaped nanoparticles of Co(OH)$_2$.

  (e) Formed nanoparticles from the Li-Fe precursor was LiFeO$_x$ (spinel or layered oxide) phase.

contact information for:
Timothy J. Boyle
Sandia National Laboratories
Advanced Materials Laboratory
1001 University Blvd. SE
Albuquerque, NM 87106
Ph. (505)272-7625 / Fx (505)272-7336
E-mail: tjboyle@Sandia.gov